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PHYSICAL REVIEW B **87**, 037401 (2013)

Comment on "Kinetics of voiding and agglomeration of copper nanolayers on silica"

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(Received 7 June 2012; published 14 January 2013)

Voiding of thin films on substrates is an important issue both for the production and the reliability of many devices and (nanotechnological) applications, like coatings for anticorrosion, wear protection, magnetic or optical properties, and decorative purposes. It is commonly accepted that grain boundary grooving plays a crucial role in the voiding process. However, in this Comment it is shown that grain boundary grooving without grain growth will usually not lead to a voiding of the film. Instead each grain develops a convex equilibrium surface that connects the neighboring grain boundaries. As the driving force for surface diffusion vanishes in this state, any further evolution based on surface diffusion stops. Often voiding does not occur, as the depth of the grooves in this state is usually smaller than the film thickness. However, it is also shown, on the basis of the same arguments, that the combination of grain growth and grain boundary grooving will eventually lead to voiding independently of the film thickness.

DOI: 10.1103/PhysRevB.87.037401 PACS number(s): 61.72.Mm, 47.20.Hw, 61.72.Cc, 68.55.−a

Saxena, Frederick, Ramanath, Gill, and Plawsky (SFRGP) described in Ref. 1 measurements of the annealing-induced voiding (dewetting) of sub-60-nm-thick Cu films on silicon dioxide. They concluded that grain boundary grooving, introduced by Mullins in 1957[2] and sketched in Fig. 1(a), is a dominating effect during the voiding of the Cu films. In particular, they stated that films thinner than 20 nm "dewet via two kinetically limiting sequential processes: void nucleation by grain boundary grooving (activation energy $E_a = 1.2\ eV$) followed by void growth and islanding through surface diffusion of Cu at the Cu-SiO_2 interface, i.e., surface spreading, (activation energy $E_a = 0.7\ eV$)", and that for films thicker than 20 nm "dewetting is governed solely by grain boundary grooving". Moreover SFRGP ruled out grain growth: "we expect that this phenomenon to be suppressed because the grain sizes in our films-verified by an independent study-are roughly of the order of the film thickness".

In the following it is pointed out that grain boundary grooving in the absence of grain growth *cannot* lead to dewetting as it was described by SFRGP. Without grain growth, grain boundary grooving will lead to the formation of an equilibrium surface, with convex grains, that corresponds to the particular morphology of the polycrystalline film. At this stage further film changes are inhibited as the driving force for grooving vanishes. However, when including also grain growth, the involved volume (mass) conservation of the film, keeping in mind the convex grain equilibrium surface, results in deeper grooves and leads eventually to voiding (dewetting).

To understand the underlying atomic mechanisms and the driving forces involved, it is important to realize that grooving does *not* involve atom diffusion along a grain boundary, although suggested at several points in the manuscript by SFRGP: examples can be found in Fig. 5 in Ref. 1, where "Atomic Transport Pathways" are indicated along the grain boundaries for both film thicknesses (in the topmost images) and where a "Kinetic bottle-neck" is indicated at the grain boundary for the thicker films (middle image). Moreover SFRGP stated that "voids nucleate at grain boundaries by Cu atom diffusion at the grain boundaries" and that for thicker films "Cu transport through the ungrooved portions of the grain boundaries (see schematic sketch in Fig. 5) constitute the kinetic bottleneck and hence grain boundary diffusion is the kinetic rate limiting process that governs complete dewetting." Finally, SFRGP reported about an "activation energy value of 1.2 eV for diffusion of Cu at grain boundaries" and stated that their experimentally determined value of "$E_a = 1.2 \pm 0.1\ eV$ is in good agreement with that of Cu grain boundary grooving".

Please note that void formation between the film and the substrate would indeed require mass transport *along* grain boundaries. However, as I will address later, the energetics in this particular case are such that void formation is prohibited. Anyhow, grain boundary grooving does not involve diffusion along a grain boundary.

As pointed out by Mullins,[2] there are two possible driving forces for grooving: evaporation-condensation and surface diffusion. As the vapor pressure of Cu at 600° C (the highest temperature used by SFRGP) is below 10^{-10} mbar, surface diffusion is the dominating driving force for grain boundary grooving. This has several implications: As the chemical potential of a surface depends on its curvature, gradients in the curvature will lead to a surface atom current that is given by the Nernst-Einstein relation[3] and that is trying to counterbalance the gradients in the curvature. The net increase/decrease of the number of atoms per unit area per unit time is proportional to the second derivative of the surface curvature. This implies that the driving force for surface diffusion vanishes and the surface is stable (no increase or decrease of atoms), if the second derivative of the surface curvature is zero. Please note that the activation barrier associated with this process is described by the surface diffusion coefficient and not a diffusion coefficient of Cu at the grain boundaries. Mullins derived his formula for grooving under the constraint of surface diffusion by assuming an infinitively large sample so that the characteristic surface profile with negative and positive surface curvature can evolve infinitely in time. It is exactly the positive surface curvature at the outer sides of the hillocks, see Fig. 1(a), that forms the driving force for grain boundary grooving. Effectively, atoms will be transported via

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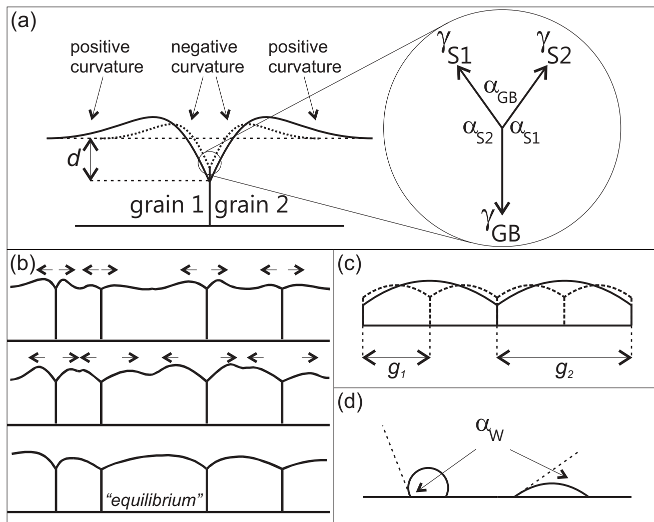

FIG. 1. (a) The equilibrium angles at a triple line are determined by the interface free energies of the surfaces and the grain boundary. The dotted surface contour represents an earlier stage of the grooving. (b) Sketch of the grooving of a polycrystalline surface for a stationary grain size configuration (no grain growth): The surface develops convex grain equilibrium shapes with respect to the given morphology of the film. Note that grooving stops. The arrows indicate the diffusion direction of the hillocks. (c) Film evolution due to an increase of the grain size: The depth of the grooves is increasing; the dashed lines represent an earlier stage. (d) Definition of the wetting angle.

surface diffusion from the surfaces with negative curvature (around the root of the groove and the hillocks) towards the outer surfaces with positive curvature (next to the hillocks). Due to the constraint of the well-defined root (dihedral) angles α_{GB} that are determined by the surface free energies γ_{S1} and γ_{S2} of the two grains and the grain boundary free energy γ_{GB}, the root becomes deeper, the hillocks become higher, and the distance between the hillocks and the root increases. However, the positive surface curvature next to the hillocks remains, although it has also increased its distance to the root. This whole process is called grooving and the driving force for further evolution is still present as long as the positive curvature next to the hillocks is present, see Fig. 1(a).

In contrast to the derivation of Mullins, who considered grooving on an infinitively large sample such that this process can continue forever, grooving dominated by surface diffusion under the constraint of fixed grain boundary positions (no grain growth) will come to rest on a polycrystalline, real sample, as grain boundaries exist next to each grain boundary under consideration. This process is sketched in Fig. 1(b). Starting with a flat, ideal surface of the polycrystalline film, grooves and corresponding hillocks will develop at each grain boundary. The dihedral angle at the different grain boundaries might be different, mostly due to the different grain boundary free energies. The positive surface curvature in the middle of each grain is the driving force for further grooving, see the middle image in Fig. 1(b). The roots become deeper, the distances between the hillocks and their grain boundaries increase, and the hillocks become higher. Eventually a surface contour with completely convex grains evolves that connects the individual grain boundaries with one another; this has been observed experimentally.[4] At this point the second derivative of the surface curvature on the grains becomes zero, the driving force for grooving vanishes, the surface is in an equilibrium state with the given morphology of the polycrystalline film, and any further evolution stops.[5]

Can this explain the dewetting (voiding) as described in the paper by SFRGP? Let us estimate the depth of the grooves considering the grain sizes provided by SFRGP and the typical ratio r of the grain boundary free energy divided by the surface free energy γ_{GB}/γ_S. With a ratio of $r = \gamma_{GB}/\gamma_S \approx 0.36$, which is usually reported for copper,[6,7] the dihedral surface angle becomes $\alpha_{GB} \approx 159^\circ$

$$\gamma_{GB}/\gamma_S \approx 2\cos(\alpha_{GB}/2). \tag{1}$$

A deviation from this dihedral surface angle as well as from the ideal convex surface of the grains has been observed to occur during and after the deposition of a polycrystalline film:[8] The reason for this existence is kinetic limitation.

Using a simple three-dimensional (3D) model, in which the grains are treated as cylinders, it is possible to determine the depth d of the groove [defined here as the distance with respect to the original, flat surface, see Fig. 1(a)] by comparing the starting situation, which is given by a flat top of the cylinder, with that of a spherical top, which describes the fully developed convex surface with constant curvature under the constraint of the dihedral surface opening angle, see Fig. 1(c). The depth d of the groove is given by

$$d = -\frac{1.15 \cdot g}{3r}\left[\frac{8}{r^2}\left(\sqrt{\left(1-\frac{r^2}{4}\right)} - 1\right) + \sqrt{1-\frac{r^2}{4}}\right], \tag{2}$$

in which $r = \gamma_{GB}/\gamma_S$ and g the grain diameter. The value of 1.15 is a correction factor that accounts for the larger distance of the corners in a hexagonal lattice. SFRGP stated that "the grain sizes in our films-verified by an independent study-are roughly of the order of the film thickness".

For a grain size of 20 nm, which represents the 20 nm thick films, the depth of the grooves is only $\approx$0.5 nm. Correspondingly, one finds a depth of $\approx$1.3 nm for a grain size (film thickness) of 50 nm. As both depths are significantly smaller than their corresponding film thickness, grain boundary grooving alone *cannot* explain voiding.

Equation (2) is an approximation, as the model neglects the energy of triple lines between three grains as well as the hexagonal grain shape (as present in the ideal case). However, a full 3D simulation that evolves the surface into an equilibrium for a hexagonal grain shape, in which α_{GB} is predefined, reveals that the depth at the triple line is only $\approx$24% deeper for a grain size of 20 nm than calculated with Eq. (2). Therefore, this formula presents a good estimate and definitively produces the right order of magnitude for the depth of the grooves. We can conclude that grain boundary grooving alone cannot explain the voiding as described by SFRGP.

However, the depth of the grooves and, therefore, the possibility for dewetting (voiding) changes dramatically when grain growth is also taken into account. For a 20-nm-thick film with a starting grain size of 20 nm, the depth of the groove is found to be $\approx$5.2 nm for grains that have developed 10 times

as large, and ≈20 nm for grain sizes that are ≈38 times as large. Similar results are obtained for a 50-nm-thick film with a starting grain size of 50 nm: The depth of the groove is ≈13 nm for grains that are 10 times as large, and ≈50 nm for grains that are ≈38 times as large. Obviously the larger the grain size is the deeper will be the groove. This effect of a combination of grain growth and grain boundary grooving is sketched in Fig. 1(c) and has been reported to occur on a polycrystalline metal film *during* annealing:[4] Grain boundary migration (grain growth) as well as the corresponding surface evolution has been observed *in situ* on an atomic scale between 293 and 748 K. Although the experiments in Ref. 4 have been performed on Au, one expects a very similar behavior for Cu, as the melting temperatures differ only 20 K on an absolute scale of 1357 K for Cu: The diffusion constants are expected, therefore, to be very similar. A deviation might come from contamination or a possible Cu-oxide layer that might have formed in the SFRGP case. However, both will only change diffusion constants[9,10] and the dihedral angle, but will not alter the general description of grain boundary grooving of polycrystalline films. We can conclude that grain boundary grooving in combination with grain growth will eventually lead to voiding (dewetting) of the film independently of the film thickness.

It is important to mention that an average grain size of ≈38 times the film thickness is usually not observed in experiments. Typical maximum grain sizes are only ≈10 times as large as the film thickness.[4,11,12] With respect to the experiments of SFRGP, one might speculate about heavily contaminated or fully oxidized grain boundaries, which might result in a higher ratio of r and, therefore, to *earlier* voiding. Indeed one finds with $r = 1$ that, for both film thicknesses, voiding sets in at a reasonable grain size of ≈13 times the film thickness. However, this choice of r is unphysical, as the grain boundary free energy is always smaller than the surface free energy. Another reason for an earlier voiding might be the shortcomings of the model, which assumes grains with equal sizes and vertical grain boundaries. As an example, abnormal grain growth involves the development of very large grains in a matrix of smaller ones. As ripening in such a situation includes material transport from the smaller grains to the larger ones, both the size and the height of the small grains is decreasing thereby enabling the possibility for voiding. Anyhow, also this scenario requires grain growth.

In the following, I would like to comment on the existence of a void between a grain boundary of the film and the substrate on which the film is deposited, as sketched in the middle, right image of Fig. 5 for the thicker films in the paper by SFRGP.[1] Whether a void is formed (or not) depends on the surface free energy of Cu, the grain boundary free energy of Cu, the surface free energy of SiO_2, and the interface free energy between Cu and SiO_2. In thermodynamic equilibrium, these free energies act like forces on the triple points (lines) leading to well-defined angles at these triple points (lines). It is straightforward to derive a stability criterion for the nucleation/growth versus shrinkage of such a void at the grain boundary-substrate interface on the basis of the dihedral surface angle α_{GB} of the grain boundary in Cu and the wetting angle, α_W [see Fig. 1(d)], for the case of Cu on SiO_2 (Ref. 13). Voids nucleate and grow only, if

$$\alpha_W > \alpha_{GB}/2 + 90^\circ. \tag{3}$$

The nucleation of voids is prohibited and existing voids will shrink if

$$\alpha_W < \alpha_{GB}/2 + 90^\circ. \tag{4}$$

As the reported wetting angles[14,15] of Cu on SiO_2, of 134° and 112.5°, are smaller than $169^\circ = (159/2 + 90)^\circ$, all existing voids should shrink and new voids should not nucleate. The above discussion is independent whether one only considers the self-diffusion of Cu on Cu or whether one also includes the diffusion of Cu across the silica surface or along the silica-Cu interface, as I considered only the energetics.

Finally, I would like to remark that grain growth, which relies on grain boundary migration and which is ruled out by SFRGP, only involves a rather small displacement of atoms across the grain boundaries. If atom diffusion along the grain boundary is assumed to be active, diffusion across the grain boundary will surely be activated and grain growth will take place.

In conclusion, grain boundary grooving in the absence of grain growth cannot explain voiding (dewetting) in the form as is suggested by SFRGP. The driving force for grain boundary grooving vanishes, when a convex equilibrium surface is formed on each grain such that the second derivative of the curvature is zero and such that it connects the neighboring grain boundaries. Without grain growth there will be no further evolution. However, when including also grain growth in this picture voiding (dewetting) is possible, as the depth of the grooves strongly depends on the evolved grain size.

The nucleation of voids between a grain boundary and the substrate depends on the grain boundary dihedral surface angle of the film and the wetting angle of the film material with the substrate. In the particular case described by SFRGP, the stability criterion reveals that voids should not nucleate and, if present at all, should shrink during the evolution.

I kindly would like to acknowledge A. Saedi for proofreading of this Comment.

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